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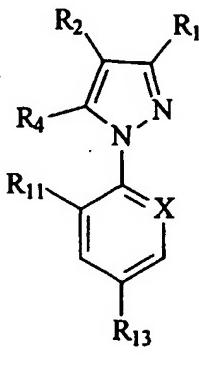
(54) Method of insect control

(57) A method of protecting a corn plant from destructive insects which comprises applying to the seed from which it grows or the soil from which the seed grows a composition comprising an insecticidal 1-arylpyrazole and an insect repellent. A composition comprising the insecticidal 1-arylpyrazole and the repellent.

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**Description**

- [0001] The present invention relates to a new method of controlling destructive insects, a new composition and a product which comprises the composition.
- 5 [0002] It is known that 5-amino-3cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole (fipronil) may be applied to corn seed at the time of planting to protect the said corn seed and the plants which emerge from the seed from *inter alia*, rootworms, e.g., *Diabrotica undecimpunctata howardi* and corn borers, e.g., *Ostrinia nubilalis*. In some cases, however, fipronil provides less than optimum activity against soil born pests, particularly against rootworms generally from the time of planting to the V6 growth stage of the corn plant.
- 10 [0003] It is also known to apply insecticidally effective amounts of pyrethroid insecticides at the time of planting to control certain pests, *inter alia*, rootworms, e.g., *Diabrotica undecimpunctata howardi*.
- [0004] An object of the present invention is to provide an improved method of control of insects, particularly insects destructive to corn.
- 15 [0005] Another object of the present invention is to provide a long-lasting control of insects destructive to corn.
- [0006] Another object of the present invention is to provide an improved method of using an insecticidal 1-arylpypyrazole.
- [0007] Another object of the present invention is to provide an improved method of using a pyrethroid insecticide.
- [0008] These and other objects are met in whole or in part by the present invention.
- [0009] The present invention provides a method of protecting a corn plant from destructive insects which method 20 comprises applying to the seed from which it grows or the soil from which the seed grows an insecticidal 1-arylpypyrazole and an insect repellent, which 1-arylpypyrazole is a compound of formula (I):



40 wherein:

- R<sub>1</sub> is CN or methyl;
- R<sub>2</sub> is S(O)<sub>n</sub>R<sub>3</sub>;
- R<sub>3</sub> is alkyl or haloalkyl;
- 45 R<sub>4</sub> is selected from the group consisting of a hydrogen atom, a halogen atom, and a radical which may be —NR<sub>5</sub>R<sub>6</sub>, —C(O)OR<sub>7</sub>, —S(O)<sub>m</sub>R<sub>7</sub>, alkyl, haloalkyl, OR<sub>8</sub>, or —N=C(R<sub>9</sub>)(R<sub>10</sub>);
- R<sub>5</sub> and R<sub>6</sub> are independently selected from a hydrogen atom, alkyl, haloalkyl, —C(O)alkyl, —S(O),CF<sub>3</sub> and —C(O)OR<sub>7</sub>; or R<sub>5</sub> and R<sub>6</sub> form together a divalent radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulphur;
- 50 R<sub>4</sub> is preferably an amino group, which is unsubstituted or which bears one or two substituents selected from the group consisting of alkyl, haloalkyl, acyl and alkoxy carbonyl;
- R<sub>7</sub> is selected from alkyl and haloalkyl;
- R<sub>8</sub> is selected from alkyl, haloalkyl and the hydrogen atom;
- R<sub>9</sub> is selected from the hydrogen atom and alkyl;
- 55 R<sub>10</sub> is selected from phenyl and heteroaryl each of which is unsubstituted or substituted by one or more hydroxy, halogen, O-alkyl, —S-alkyl, cyano, or alkyl or combinations thereof;
- X is selected from the nitrogen atom and the radical C—R<sub>12</sub>;
- R<sub>11</sub> and R<sub>12</sub> are independently selected from a halogen atom and the hydrogen atom;

$R_{13}$  is selected from a halogen atom, haloalkyl, haloalkoxy,  $S(O)_qCF_3$  and  $-SF_5$ , preferably from a halogen atom, haloalkyl, haloalkoxy,  $-SF_5$ ;

$m, n, q, r$  are independently selected from 0, 1 and 2;

provided that when  $R_1$  is methyl,  $R_3$  is haloalkyl,  $R_4$  is  $NH_2$ ,  $R_{11}$  is Cl,  $R_{13}$  is  $CF_3$ , and X is N. The 1-arylpypyrazole and insect repellent are generally applied in a composition comprising them.

[0010] The alkyl and alkoxy groups of the formula (I) are preferably lower alkyl and alkoxy groups, that is, radicals having one to four carbon atoms. The haloalkyl and haloalkoxy groups likewise preferably have one to four carbon atoms. The haloalkyl and haloalkoxy groups can bear one or more halogen atoms; preferred groups of this type include  $-CF_3$  and  $-OCF_3$ . It is to be understood that the ring formed by the divalent alkylene radical represented by  $R_5$  and  $R_6$  and including the nitrogen atom to which  $R_5$  and  $R_6$  are attached is generally a 5, 6, or 7-membered ring. When  $R_{10}$  is heteroaryl, it is preferably pyridyl, most preferably 2-pyridyl. It is to be understood that the 1-arylpypyrazoles of formula (I) include enantiomers and/or diastereomers thereof.

[0011] The preparation of compounds of formula (I) can be effected according to any process described in International Patent Publications No. WO 87/03781, WO 93/06089 and WO 94/21606, as well as in European Patent Publication numbers 0295117, 0403300, 0385809 and 0679650, German Patent Publication 19511269 and United States Patents 5,232,940 and 5,236,938.

[0012] Preferably the compound of formula (I) has one or more of the following features:

- 20       $R_1$  is CN;
- $R_4$  is  $-NR_5R_6$ ;
- $R_5$  and  $R_6$  are independently selected from the hydrogen atom, alkyl, haloalkyl,  $-C(O)alkyl$ ,  $C(O)OR_7$ ;
- X is  $C-R_{12}$ ; or
- $R_{13}$  is selected from a halogen atom, haloalkyl, haloalkoxy and  $SF_5$ .

[0013] Most preferably the compound of formula (I) is 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethyl(phenyl)-4-trifluoromethylsulfinyl)pyrazole (i.e. fipronil) or 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-ethylsulfinylpyrazole hereinafter known as Compound B.

[0014] In a preferred embodiment, the repellent is applied in a substantially non-lethal amount. By the term "substantially non-lethal" is meant an amount, which when delivered to the soil alone kills less than 10% of the pests so-controlled by the method of the invention. Preferably the repellent kills less than 5% of the pests.

[0015] The repellent may be a known insect repellent. Preferably the insect repellent is a pyrethroid insecticide. Preferably, the repellent is a pyrethroid insecticide that is selected from the group consisting of tefluthrin, permethrin, fenvalerate, esfenvalerate, cypermethrin, cyhalothrin, lambda-cyhalothrin, bifenthrin and deltamethrin.

[0016] Generally the pests controlled by the method include *Agrotis spp.*, e.g. Black cutworm, rootworms, including *Diabrotica spp.*, e.g. *Diabrotica undecimpunctata howardi* or *Diabrotica virgifera*; or corn seed maggot, e.g. *Hylemya platura*, *Chortophila platura*, *Chortophila cilicrura*, *Hylemya cilicrura*, *Phorbia platura*, *Chortophila funesta*, *Chortophila fusciceps*, *Crinura cilicrura*, *Crinura platura*, *Crinura fusciceps*, *Crinura funesta*, *Delia cilicrura*, *Delia funesta*, *Delia fusciceps*, *Hylemya funesta*, *Hylemya fusciceps*, *Phorbia cilicrura*, *Phorbia funesta*, *Phorbia fusciceps*, *Hylemya cana*, *Delia cana*, *Hylemya cana*, or *Delia platura*.

[0017] Generally, the weight to weight ratio of the insecticidal 1-arylpypyrazole to the repellent is from 2:1 to 200:1, preferably from 5:1 to 75:1, most preferably from 8:1 to 50:1.

[0018] The composition is generally applied as a liquid composition to the soil or as a seed treatment to the seed from which the corn plant grows.

[0019] In a highly preferred embodiment, the liquid composition may be directed into the soil mixing zone below the level of the top of a furrow in which the corn seed may be planted. In this way, the composition may be incorporated in the soil below the level of the soil, on the seed and above the seed as the furrow is closed. The application spray can be a stream of liquid or a conical spray.

[0020] Generally, the volume of liquid to be used per unit land area is from 0.1 to 50 gallons per acre (0.9 to 470 L/ha), preferably from 0.2 to 10 gal/A (1.9-90 L/ha), more preferably from 0.5 to 5 gal/A (4.7—47 L/ha), most preferably from 1 to 3 gal/A (9.4—28 L/ha).

[0021] When the repellent is a pyrethroid insecticide, it is preferably used at about 1% to 90% of the labelled insecticidal use rate, preferably from 5% to 50%. The following table provides a general guidance to preferred rates to be used in the method of the present invention.

Repellent	Current Field Use Rate in Corn (lb.ai/acre)	Use rate according to the present invention (lb. ai/acre)
tefluthrin	0.075 - 0.15	0.001 - 0.02
esfenvalerate	0.03 - 0.05	0.001 - 0.02
lambda-cyhalothrin	0.015 - 0.030	0.001 - 0.01
permethrin	0.1 - 0.2	0.01 - 0.02
cyfluthrin	not labelled	0.001 - 0.05

- 15 [0022] The abbreviation "ai" means active ingredient.
- [0023] The rate of use of the 1-arylpyrazole is generally from 0.01 lb. per acre (11 g per hectare) to about 2.2 lb./acre (1000 g/Ha), preferably from 20 to 200 g/Ha.
- 20 [0024] In a highly preferred embodiment of the invention, the composition is applied when the soil temperature is from 4°C to 25°C, preferably from 10°C to 20°C. In this way there is a better insecticidal effect on the above insect species than with the 1-arylpyrazole insecticide alone.
- 25 [0025] The present invention also provides an agriculturally acceptable composition for protecting corn plants from destructive insects which comprises an insecticidal 1-arylpyrazole as defined above and a repellent, preferably a substantially non-lethal amount of an insect repellent as defined above. The composition may be, for example, a liquid composition or a granular composition, preferably a liquid composition in use. Liquid compositions include those known to the skilled addressee and emulsifiable concentrates, suspension concentrates or aqueous emulsions are generally preferred.
- 30 [0026] The present invention also provides a product comprising an insecticidal 1- arylpyrazole as defined above and a repellent for simultaneous, separate or sequential use in the control of destructive insects of corn on or on the soil from which the corn grows. Preferably the product may be a premixed product which comprises both the 1-arylpyrazole and the repellent.
- [0027] The following non-limiting example illustrates the invention:

Example 1:

- 35 [0028] Corn seed is planted in a field where the average temperature of the soil is about 10°C. As the corn seed is planted, fipronil (as the commercial product Regent® 80WG) and lambda-cyhalothrin (as the commercial product Warrior®) are applied simultaneously on the seed as a liquid composition in water at rates of 0.13 lbs/acre (0.15 kg/Ha) and 0.01 lbs/acre (0.011 kg/Ha) respectively. One part of the field is treated with Regent 80WG at 0.13 lbs./acre alone. After 40 4 weeks, several plants are removed to determine the damage to the roots and stalks. The treatment with fipronil and lambda-cyhalothrin provides a lower numerical Iowa Root rating than the treatment with Regent alone. There is less damage from black cutworm in the fipronil + lambda cyhalothrin treatment than in the fipronil treatment.

Example 2:

- 45 [0029] The procedure of Example 1 is used with fipronil (as the commercial product Regent® 4SC) and Cyfluthrin (as the commercial product Baythroid®) at rates of 0.13 lbs/acre (0.15 kg/ha) and 2.6 ounces product/acre (0.023 kg/ha). One part of the field is treated with Regent® 4SC at 0.13 lbs/acre (0.15 kg/ha) alone and another part of the field is treated with Baythroid® at 2.6 ounces product/acre (0.023 kg/ha) alone.
- 50 [0030] Toward the end of the growing season, the plants are removed to determine damage to the roots. The following results are observed.

TREATMENT	IOWA ROOT RATING
Regent 4SC	3.4

(continued)

TREATMENT	IOWA ROOT RATING
Baythroid	4.2
Regent + Baythroid	2.6

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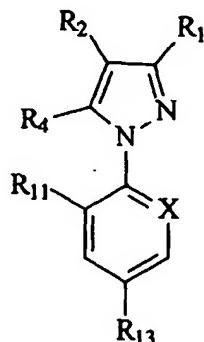
[0031] While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims, including equivalents thereof.

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## Claims

- 15 1. A method of protecting a corn plant from destructive insects which method comprises applying to the seed from which it grows or the soil from which the seed grows an insecticidal 1-arylpypyrazole and an insect repellent, which 1-arylpypyrazole is a compound of formula (I):

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(I)

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wherein:

- 40 R<sub>1</sub> is CN or methyl;  
 R<sub>2</sub> is S(O)<sub>n</sub>R<sub>3</sub>;  
 R<sub>3</sub> is alkyl or haloalkyl;  
 R<sub>4</sub> is selected from the group consisting of a hydrogen atom, a halogen atom, and a radical which may be —NR<sub>5</sub>R<sub>6</sub>, -C(O)OR<sub>7</sub>, -S(O)<sub>m</sub>R<sub>7</sub>, alkyl, haloalkyl, or OR<sub>8</sub>, or —N=C(R<sub>9</sub>)(R<sub>10</sub>);  
 R<sub>5</sub> and R<sub>6</sub> are independently selected from a hydrogen atom, alkyl, haloalkyl, -C(O)alkyl, -S(O)<sub>r</sub>CF<sub>3</sub> and —C(O)OR<sub>7</sub>; or R<sub>5</sub> and R<sub>6</sub> form together a divalent radical which may be interrupted by one or more heteroatoms;  
 R<sub>4</sub> is preferably an amino group, which is unsubstituted or which bears one or two substituents selected from the group consisting of alkyl, haloalkyl, acyl and alkoxy carbonyl;  
 R<sub>7</sub> is selected from alkyl and haloalkyl;  
 45 R<sub>8</sub> is selected from alkyl, haloalkyl and the hydrogen atom;  
 R<sub>9</sub> is selected from the hydrogen atom and alkyl;  
 R<sub>10</sub> is selected from phenyl and heteroaryl each of which is unsubstituted or substituted by one or more hydroxy, halogen, O-alkyl, -S-alkyl, cyano, or alkyl or combinations thereof;  
 X is selected from the nitrogen atom and the radical C-R<sub>12</sub>;  
 50 R<sub>11</sub> and R<sub>12</sub> are independently selected from a halogen atom and the hydrogen atom;  
 R<sub>13</sub> is selected from a halogen atom, haloalkyl, haloalkoxy, S(O)<sub>q</sub>CF<sub>3</sub> and —SF<sub>5</sub>, preferably from a halogen atom, haloalkyl, haloalkoxy, -SF<sub>5</sub>;  
 m,n,q,r are independently selected from 0,1 and 2;

provided that when R<sub>1</sub> is methyl, R<sub>3</sub> is haloalkyl, R<sub>4</sub> is NH<sub>2</sub>, R<sub>11</sub> is Cl, R<sub>13</sub> is CF<sub>3</sub>, and X is N.

- 2. The method according to claim 1 wherein the repellent is an insecticide applied in a substantially non-lethal amount.
- 5      3. The method according to claim 1 or claim 2 wherein the repellent is a pyrethroid insecticide.
- 10     4. The method according to claim 3 wherein the repellent is a pyrethroid insecticide which is selected from the group consisting of tefluthrin, permethrin, fenvalerate, esfenvalerate, cypermethrin, cyhalothrin, lambda-cyhalothrin, bifenthrin and deltamethrin.
- 15     5. The method according to any one of the foregoing claims wherein the insect is *Agrotis spp.*, preferably black cut-worm; a rootworm, preferably *Diabrotica spp.*, more preferably *Diabrotica undecimpunctata howardi* or *Diabrotica virgifera*; or corn seed maggot, preferably *Hylemya platura*, *Chortophila platura*, *Chortophila cilicrura*, *Hylemya cilicrura*, *Phorbia platura*, *Chortophila funesta*, *Chortophila fusciceps*, *Crinura cilicrura*, *Crinura platura*, *Crinura fusciceps*, *Crinura funesta*, *Delia cilicrura*, *Delia funesta*, *Delia fusciceps*, *Hylemya funesata*, *Hylemya fusciceps*, *Phorbia cilicrura*, *Phorbia funesta*, *Phorbia fusciceps*, *Hylemya cana*, *Delia cana*, *Hylemya cana*, or *Delia platura*.
- 20     6. The method according to any one of the foregoing claims wherein the 1-arylpypyrazole has one or more of the following features:
- 25        R<sub>1</sub> is CN;  
R<sub>4</sub> is —NR<sub>5</sub>R<sub>6</sub>;  
R<sub>5</sub> and R<sub>6</sub> are independently selected from the hydrogen atom, alkyl, haloalkyl, -C(O)alkyl, C(O)OR<sub>7</sub>;  
X is C—R<sub>12</sub>; or  
R<sub>13</sub> is selected from a halogen atom, haloalkyl, haloalkoxy and —SF<sub>5</sub>.
- 30     7. The method according to any one of the foregoing claims wherein the insecticidal 1-arylpypyrazole is 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole.
- 35     8. The method according to any one of the foregoing claims wherein the weight to weight ratio of the insecticidal 1-arylpypyrazole to the repellent is from 2:1 to 200:1, preferably from 5:1 to 75:1, most preferably from 8:1 to 50:1.
- 40     9. The method according to any one of the foregoing claims wherein the composition is applied when the soil temperature is from 4°C to 25°C, preferably from 10° to 20°C.
- 45     10. The method according to any one of the foregoing claims wherein the insecticidal 1-arylpypyrazole is applied at a rate of from 11 grams per hectare to about 1000 gha.
- 11. An agriculturally acceptable composition for protecting corn plants from destructive insects which comprises an insecticidal 1-arylpypyrazole as defined in any one of the foregoing claims and an insect repellent as defined in any one of the foregoing claims, in association with an agriculturally acceptable carrier.
- 12. A product comprising an insecticidal 1-arylpypyrazole as defined in any one of the foregoing claims and an insect repellent as defined in any one of the foregoing claims for simultaneous, separate or sequential use in the control of destructive insects of corn in or on the soil from which the corn grows.
- 13. The product of claim 12 which is a premixed package of the insecticidal 1-arylpypyrazole and the repellent.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 31 0583

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
X	WO 95 22902 A (RHONE POULENC AGROCHIMIE ;KODAMA HIROSHI (JP); WADA YASUHIRO (JP);) 31 August 1995 * page 4, line 5-18; examples 1-3; table 1 *	11-13	A01N43/56 A01N53/00 //(A01N43/56, 53:00)
Y	US 5 516 787 A (TAKADA YOJI) 14 May 1996 * column 2, line 43-56 *	1-10	
D,Y	WO 93 06089 A (ICI PLC) 1 April 1993 * page 8, paragraph 3-6 *	1-10	
Y	C. D. S. TOMLIN (ED.): "The Pesticide Manual" 1997 , BRITISH CROP PROTECTION COUNCIL , FARNHAM XP002103044 page 545 - 547: Fipronil: 'Applications'.	1-10	
TECHNICAL FIELDS SEARCHED (Int.Cl.)			
A01N			
The present search report has been drawn up for all claims			
Place of search  EPO FORM 1500 (03-92) (P01/01)	Date of completion of the search  MUNICH 18 May 1999	Examiner  Klaver, J	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background D : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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18-05-1999

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9522902	A	31-08-1995		AU 679622 B AU 1810495 A BR 9507118 A CA 2183341 A CN 1141580 A EP 0746205 A JP 7285813 A US 5747519 A ZA 9501611 A	03-07-1997 11-09-1995 12-08-1997 31-08-1995 29-01-1997 11-12-1996 31-10-1995 05-05-1998 07-12-1995
US 5516787	A	14-05-1996		JP 7173021 A BR 9405163 A CN 1106993 A ES 2108619 A FR 2713891 A IT T0941036 A US 5629334 A	11-07-1995 17-10-1995 23-08-1995 16-12-1997 23-06-1995 20-06-1995 13-05-1997
WO 9306089	A	01-04-1993		AT 163180 T AU 664199 B AU 2541392 A AU 692902 B AU 3051295 A BR 9206552 A CA 2119385 A CN 1071163 A,B CN 1115205 A CZ 9400712 A DE 69224437 D DE 69224437 T EP 0605469 A ES 2112913 T GR 3026099 T HU 66735 A,B JP 7500319 T MX 9205468 A NZ 244265 A TR 26511 A US 5451598 A ZA 9206785 A	15-02-1998 09-11-1995 27-04-1993 18-06-1998 23-11-1995 17-10-1995 01-04-1993 21-04-1993 24-01-1996 13-07-1994 19-03-1998 04-06-1998 13-07-1994 16-04-1998 29-05-1998 28-12-1994 12-01-1995 01-03-1993 28-03-1995 15-03-1995 19-09-1995 09-06-1993